Thermal desorption modulation for comprehensive two-dimensional gas chromatography using a simple and inexpensive segmented-loop fluidic interface

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ABSTRACT

In this study, we introduce a modulation strategy for comprehensive two-dimensional gas chromatography (GC×GC) by using a simple and consumable-free modulator. This "Do-It-Yourself" interface comprised a 1.0 m×0.25 mm segment of MTX-5 metallic column and a low-cost DC power supply. Thermal desorption modulation (TDM) was attained using a dual-stage heater-based modulator in a novel segmented-loop configuration. TDM was achieved by alternating analyte trapping and thermal desorption. Former process relied on analyte partition to sorbent phase, while latter explored direct resistive heating. Introduction of an intermediate delay segment between the two stages mitigated analyte breakthrough, improving peak symmetry and chromatographic efficiency. This feature was critical to acquire reliable GC×GC modulation using such simple heater-based device. The effects of important modulation variables on 2D separations were investigated, including TDM stage length, dimension of delay loop, and outlet pressure. Significant advances and limitations of proposed TDM strategy were carefully determined. Proposed GC×GC prototype by using an in-oven TDM modulator was successfully applied to a series of challenging matrices, including petroleum distillates, biodiesel, and essential oil. This open-hardware, cost-effective modulator was easy to install and operate, as it circumvented the need for sophisticated components (e.g. moving parts and cooling systems). Therefore, our modulator is a compelling alternative to existing GC×GC solutions to operate in resource-limited laboratories.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC×GC) is currently one of the most effective instrumental techniques for the separation of volatile and semi-volatile organic compounds [1]. The multidimensional process is achieved by combining two gas chromatographic separations with different selectivities (i.e. solvation properties) [2]. Such two stages are interfaced in a sequential fashion using a modulator [3]. Furthermore, the experiments are designed to preserve the separation attained in each dimension. Several successful applications of GC×GC to petrochemical [4], forensics [5], and food analyses [6] have been reported.

The most valuable component of any GC×GC platform is the modulator [7]. Thermal modulators are largely divided into heater-based and cryogenic-dependent interfaces. Cryogenic-based interfaces dominate today's GC×GC instruments, due to efficient thermal modulation and unparalleled experimental flexibility. Nevertheless, systems' dependence on cryogenic fluid eclipses adoption of GC×GC by resource-limited facilities and hinders on-field applications. Hence, much research has been dedicated to the development of cost-effective and consumable-free modulators.

Modulation in heater-based devices rely on thermal desorption [8] and operate in a similar manner to trapping systems commonly used for concentrating volatile organic compounds (VOC) [9]. Such interfaces trap primary column effluent (^{1}D), at or above ambient temperatures, using a sorbent material (e.g. thick stationary phase) that retains VOC, but does not retain permanent gases, like H_2, N_2, CO_2. Then, trapped analytes are desorbed by applying heat and flushed downstream to the second separation stage (^{2}D) [8,9]. In GC×GC experiments these stages are continuously alternated to obtain analyte modulation. In addition, sampling frequency of the modulator is defined by the modulation period.

Thermal desorption modulation (TDM) was introduced by Phillips and coworkers in the early 90′s [10]. In the original design, the modulation section consisted of the initial 15 cm of the secondary capillary column. Such loop-like structure was coated with gold-based paint to perform resistive heating. The interface was positioned outside the chromatographic oven and used two adjacent TDM stages. Thus, attained modulation alternated analyte trapping / focusing, using a sorbent phase, and thermal desorption, by applying electrical current through the metal coating. However, sample breakthrough and band broadening limited such setup [8]. In addition, decreased coating longevity severely limited apparatus robustness [10,11].

The rotating thermal modulator, introduced in 1996, was the first commercial interface for GC×GC [12]. Such device used a slotted heater to "sweep" analytes downstream over the modulation capillary [8]. The slotted heater operated at 100ºC above GC oven temperature to attain GC×GC modulation. Thus, a thick sorbent phase combined with periodical thermal sweeping enabled successful TDM in some applications [13]. Alternatively, a steel jacket-based TDM interface using indirect resistive heating and non-moving parts was also proposed to mimic the operating principle of the sweeper. In the latter setup, GC×GC separations were produced using an array of 10 adjacent stages per modulation.

In TDM, effective analyte trapping requires precise balancing of factors that contribute to analyte partition into stationary phase, like film thickness and sorbent operating temperature. Over the past decade, a significant number of reports mitigated such issue using an active cooling unit to favor analyte partition, instead of exploring thick sorbent coatings for TDM [14–16]. Such setups, however, required sophisticated assemblies for efficient heat transfer using thermoelectrical cooling units (e.g. Peltier effect) to avoid the use of cryogenic fluids [16–20]. In this context, concurrent routes are urgently needed to provide cost-effective and robust interfaces for GC×GC separations.

In an effort to address aforementioned restrictions, we report the development of a simple and inexpensive TDM interface for conventional GC×GC separations. This novel heater-based modulator used two independent stages segmented by a 60 cm delay loop. Each stage consisted of 20 cm portion of a metallic modulation capillary, which were powered by a low-cost DC power supply. In this interface, analyte trapping was attained by partition into a 0.5 µm low-selectivity sorbent phase. Analyte desorption was readily produced by direct resistive heating. Furthermore, this unique segmented-loop configuration mitigated analyte breakthrough and enhanced peak symmetry. Important GC×GC modulation variables were carefully studied, including stage length, dimension of delay loop, and outlet pressure. Moreover, the effects of ambient and vacuum outlet pressure were determined by GC×GC experiments with flame ionization detection (GC×GC-FID) and coupling to mass spectrometry (GC×GC-MS), respectively. Proposed GC×GC prototype using an in-oven modulator was applied to a series of demanding applications from oil & gas industry and food chemistry. To the best of our knowledge, this "Do-It-Yourself" prototype is the simplest heater-based modulator reported, as it bypassed the use of sophisticated components (e.g. cooling systems and moving parts).

2. Materials and methods

2.1. Reagents and samples

All samples were prepared using HPLC-grade *n*-heptane (Sigma-Aldrich – Bellefonte, PA, USA). Dodecane (CAS 112-40-3), naphthalene (CAS 91-20-3), and linalool (CAS 78-70-6) were purchased from Supelco (Bellefonte, PA, USA). Petroleum distillate samples were collected from fueling stations in the Campinas area (São Paulo, Brazil). Hop oil was kindly provided by the São Carlos Institute of Chemistry (IQSC-USP – São Carlos, SP, Brazil). The GLC-85 fatty acid methyl ester standard mixture was provided by Nu-Chek Prep, Inc. (Elysian, MN, USA).

The adjustable ITFA 5020 DC power supply (Instrutemp – São Paulo, SP, Brazil) was used for TDM optimization. A low-cost 5 V/45 W DC power supply was used to build the latest version of the modulator (Eletrônica Esteves – Urupês, SP, Brazil).

2.2. Gas chromatography

The GC×GC-FID prototype was assembled on a Thermo Trace 1310 Series GC-FID. Such instrument was fitted with a split/splitless injector. Hydrogen was used as carrier gas at 0.8 mL min^{-1}. Data acquisition was performed at 120 Hz. Both injector and detector operated at 250 ºC.

The GC×GC-MS experiments were executed on a Shimadzu QP2010 Ultra GC-MS (Kyoto, Japan). This equipment was fitted with a split/splitless injector. Helium was used as carrier gas at 1.0 mL min^{-1}. Data acquisition was performed at 25 scan s^{-1} along the m/z range of 40 – 500. Ion source and MS transfer line were kept at 200 ºC and 250 ºC, respectively.

Column set comprised a 30 m×0.25 mm MEGA-5HT (0.15 µm film thickness) primary column (MEGA snc – Legnano, MI, Italy) and a 1.0 m×0.10 mm TG-WAXMS (0.10 µm film thickness) secondary column (Thermo Fischer – Waltham, MA, USA). Metallic modulation loop consisted of a 1.0 m×0.25 mm MTX-5 (0.50 µm film thickness) column (Restek Corporation – Bellefonte, PA, USA). The column set was connected using two low-dead volume SilTite µ-unions (SGE Analytical – Ringwood, VIC, Australia).

Our segmented loop-based TDM interface, as shown in Fig. 1, was installed inside the GC oven to bypass the need for heated transfer lines and custom parts. This interface comprised a metallic capillary (Fig. 1B) column and a DC power supply (Fig. 1C). The MTX-5 modulation loop was fixed in a 100 µm Kapton sheet and arranged in a loop configuration [21] to mitigate analyte breakthrough. The two TDM stages were created by delimiting the metallic column using the electrical connections (Fig. 1B). Moreover, these stages were of identical length (L_{stage}). Inputting of a delay loop (L_{delay}) between the two stages produced the segmented loop configuration for TDM. During GC×GC optimization, values of L_{stage} and L_{delay} varied from 10 to 25 cm and 0 to 70 cm, respectively. Best modulation was achieved by using L_{stage}=20 cm and L_{delay}=60 cm.

Analyte desorption was attained by applying heat loads of 16 J to each TDM stage. Noteworthy, identical GC×GC results may be accomplished by either using an adjustable or fixed DC power supply. When using the adjustable power supply, evaluation of constant desorption pulses and varying source voltage/current are recommended. So, optimal TDM modulation was obtained with 32 W and 500 ms heat pulses. Conversely, values of desorption pulses must be varied with fixed power supply to study TDM conditions. In this case, modulation was achieved with 355 ms of desorption pulses by using the low-cost 45 W power source.

Modulation events were controlled using a low-cost Arduino Uno microcontroller (Ivrea, Italy) [22–24]. Full hardware setup is presented in Fig. S1. Internal counter used 16-bit hardware on ATmega328. The basic wiring-program is described in Supplementary Data. Synchronization of modulation sequence and GC analysis was attained by analogic monitoring of instrument's remote control. GC Image (Zoex Corporation – Lincoln, NE, USA) was used for data visualization. In addition, an illustration of the GC×GC-FID prototype is provided in Fig. S2.

3. Results and discussion

Modulators are unique to GC×GC experiments and remain the subject of intense development in hardware [2]. Efficient band sampling and transfer is required to attain increased peak capacity in any GC×GC separation. Herein, we portray a simple consumable-free TDM system fabricated to generate ^{2}D separations with modulation